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RESEARCH ARTICLE

Sorption of selected pharmaceuticals by a river sediment: role and mechanisms of sediment or Aldrich humic substances

Thibaut Le Guet[1] · Ilham Hsini[1] · Jérôme Labanowski[1] · Leslie Mondamert[1]

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Abstract

Sorption of pharmaceuticals onto sediments is frequently related to organic matter content. Thus, the present work aimed to compare the effect of humic substances (HS) extracted from a river sediment versus Aldrich (HS) on the sorption of selected pharmaceuticals onto this river sediment. The results exhibited no "unique" effect of the presence of HS from the same origin. Thus, the sediment HS increased the sorption of sulfamethoxazole (SMX), diclofenac (DCF), and trimethoprim (TMP), but reduced the sorption of atenolol (ATN). The presence of Aldrich HS increased the sorption of TMP and ATN and decreased the sorption of SMX and DCF. Fluorescence quenching measurements revealed that these effects cannot be explained only by the presence of pharmaceutical HS associations. The use of several sorption models suggested that the sorption of SMX, DCF, and ATN involves multilayer mechanisms. Furthermore, it was pointed out that the presence of HS does not change the sorption mechanisms although it was observed interaction between HS and the sediment. Indeed, the sediment HS sorbs onto the sediment whereas the Aldrich HS tends to mobilize organic compounds from the sediment to the solution.

Keywords Pharmaceuticals · Sediments · Sorption · Organic matter · Humic substances · Association

Introduction

A large number of pharmaceutical compounds are regularly found in surface water and groundwater samples (Aga 2007; Barnes et al. 2008). Through a comprehensive literature review of publications and review articles, Aus der Beek et al. (2016) showed that pharmaceuticals or their metabolites and transformation products have been detected in the environment of 71 countries covering all continents. The dissemination of pharmaceuticals is now unanimously considered as an essential environmental health issue (Bradley et al. 2016), and some compounds have been proposed to be added to the "priority substances watchlists" (de Voogt et al. 2009; Environmental Protection Agency U.S. 2012; European Commision 2013). Despite the low concentrations of pharmaceuticals generally observed into the environments (nb. from ng L^{-1} to μg L^{-1} in natural waters (Aga 2007)), some adverse effects have been reported in freshwater or marine ecosystems. For example, the study of Pinckney et al. (2013) reported that the exposure of benthic microalgal communities in the North inlet estuary (USA) to tylosin (an antimicrobial) in sediments resulted in reduction of microalgal biomass and primary productivity and retarded diatom growth. Some neuroactive pharmaceuticals have also seemed to alter the reproductive behavior of fish leaving fear a potential decrease of their populations. Diclofenac, a widely used non-steroidal anti-inflammatory drug, has been shown to damage the gills and lungs of fish (Gilbert 2012). Furthermore, the question of the possible chronic exposure of humans to pharmaceuticals is increasingly raised (Mennigen et al. 2011) since many pharmaceuticals have been also detected in tap/drinking waters (Aga 2007; Padhye et al. 2014).

This large presence of pharmaceuticals into the environment is mainly attributed to wastewater discharges, although emissions from industrial production, hospitals, agriculture, and aquaculture are important locally (Chonova et al. 2017). Indeed, conventional wastewater treatment plants (WWTP)

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✉ Leslie Mondamert
leslie.mondamert@univ–poitiers.fr

[1] UMR IC2MP 7285, CNRS/Université de Poitiers, ENSIP, TSA 41105, 1 rue Marcel Doré, 86073 Poitiers, Cedex 9, France

are unable to completely remove most of the pharmaceuticals. For example, the removal of carbamazepine is close to 3.5% but reaches 99.9% for paracetamol (Chonova et al. 2016). Furthermore, the efficiency of the pharmaceutical removal is strongly dependent on the treatment technology. In general, the WWTP involving trickling filter beds resulted in less than 70% removal, while the WWTP using activated sludge treatment gave a much higher removal efficiency of over 85% (Kasprzyk-Hordern et al. 2010). Currently, many WWTP in Europe are being equipped with ozonation or activated carbon processes to effectively reduce pharmaceutical residues (Okuda et al. 2008).

Once in the environment, various processes control the fate of pharmaceuticals. In surface waters, it was widely shown that biotransformation, photolysis, and sorption to sediments and biofilms are the most important (Ramil et al. 2010; Radke et al. 2010; Kunkel and Radke 2012; Li et al. 2016). They can occur on "free" pharmaceuticals or on their associated form. Indeed, pharmaceuticals can be associated with dissolved organic matter (Hernandez-Ruiz et al. 2012; Peng et al. 2014), ions (Kümmerer 2009), or suspended particles such as clays, silts, or oxides (Bekçi et al. 2006; Avisar et al. 2010). The accumulation of pharmaceuticals in waters or in sediments appears the pathway of highest importance (Radke and Maier 2014), although microbial transformations largely contribute to their removal (Lewandowski et al. 2011; Riml et al. 2013; Li et al. 2016). Sediment particles are over time a reservoir for the accumulation of pharmaceuticals in freshwater ecosystems and can act as a secondary pollution source from which pharmaceuticals can be released by changes in environmental conditions (e.g., pH and salinity) (Liang et al. 2013). Contaminated sediments can be also resuspended during storm events, re-exposing aquatic biota to these compounds (Gaw et al. 2014).

Typical concentrations observed in river sediments generally range from nanograms per gram to several micrograms per gram (Kümmerer 2009). Several pharmaceutical compounds belonging to different therapeutic groups (analgesics and anti-inflammatory drugs, anti-ulcer agent, psychiatric drugs, antiepileptic drug, antibiotics, ß-blockers, diuretics, lipid regulator and cholesterol lowering statin drugs, and anti-histamines) have been detected in surface sediments or sediment cores (Tamtam et al. 2011; Matongo et al. 2015; Radović et al. 2016). Thus, 34 pharmaceutical compounds have been found in sediments of the Ebro river in northeast of Spain (da Silva et al. 2011). Zhou et al. (2011) and Hu et al. (2012) found until 17 common antibiotics (including fluoroquinolones, tetracyclines, sulfonamides, and macrolides) in the sediments of the Yellow River, Hai River, Liao River, or Dagu River in northern China. Various estrogens (diethylstilbestrol, estrone, β-estradiol, estriol, 17α-ethynylestradiol, and β-estradiol 17-valerate) were also identified in sediments from three rivers in Tianjin area in China (Lei et al. 2009). Varga et al. (2010) found many acidic pharmaceuticals (ibuprofen, naproxen, ketoprofen, and diclofenac) in the Danube river sediments in Budapest (Hungary). Other recent studies on sediments also highlight that both parent compounds and transformation products or metabolites are currently found in sediments. Thus, dehydrated erythromycin (nb. the main gastric metabolite of erythromycin) was found in San Francisco Bay in the USA (3.4 ng g^{-1}) (Klosterhaus et al. 2013) and in the Pearl River estuary in China (0.7–14 ng g^{-1}) (Liang et al. 2013). Langford and Thomas (2011) reported also traces of α-hydroxy metoprolol (1–3 ng g^{-1}) and simvastatin hydroxy carboxylic acid (2–4 ng g^{-1}) in sediments collected from fjord in Norway.

The sorption and mobility of pharmaceuticals have been frequently related to the presence of organic matter. Thus, Varga et al. (2010) indicated that accumulation of pharmaceuticals in sediments depends on the pharmaceutical concentration in aqueous phase, the properties of the compound (solubility, pKa, and log Kow), and the total organic carbon content of the sediment. Li and Zhang (2016) observed that the adsorption of oxytetracycline on sediments is strongly related to the organic carbon (OC) content. Lai et al. (2000) found also a strong correlation between sorption of estrogens and total organic carbon content. There is also other evidence that different processes involving sediment organic matter (e.g., hydrophobic partitioning, hydrogen bonding, and interactions between π-electrons) contribute to the sorption of steroid hormones in sediments (Aga 2007). Several authors have pointed out that most of pharmaceuticals can also bind with dissolved organic matter (DOM) because of the presence of a wide diversity of functional groups (Yamamoto et al. 2003; Gu et al. 2007; Sun et al. 2007; Bai et al. 2008). However, only few studies have shown that sorption is related not only to DOM content but also to the composition and consequently the origin of the OM. Oh et al. (2016) investigated the effect of dissolved organic matter model compounds (citrate and urea) on the ibuprofen sorption in sediments. They observed that the presence of citrate hinders the sorption of ibuprofen but urea did not. Moreover, the humic substances (HS) play also a critical role in sorption of pharmaceuticals (such as endocrine disruptors). Sun et al. (2006) showed that the Koc values for HS are comparable with the Koc values for raw sediments and highly dependent on the physicochemical properties of HS.

In surface waters, the composition of DOM may have to change with seasons or with storm/run off events in watershed. However, the effect of changes in the origin of DOM is not well understood, especially for the sorption of pharmaceuticals onto sediments. Thus, the present work proposed to compare the effect of humic substances extracted from a river sediment versus Aldrich humic substances on the sorption of selected pharmaceuticals (sulfamethoxazole, diclofenac, atenolol, and trimethoprim) onto this sediment. The study of classical sorption models and fluorescence quenching measurements was used to unravel the sorption mechanisms.

Materials and methods

Sediment collection and preparation

About 60 L of a river sediment was collected in the Clain river upstream the city of Poitiers (France; GPS coordinates 46.53994, 0.330248). The sediment was frozen at − 80 °C, freeze-dried, passed through a 630-μm Ø sieve to remove debris, and then stored in sealed amber glass bottles at room temperature before use. The main physical and chemical properties of this sediment are given in Table SI-1 (in supplementary material). Briefly, the Clain sediment is characterized by a pH of 7.1, a sandy loam texture, and a high content in calcium carbonate (37 ± 4%) and organic matter (18 ± 3%).

Chemicals and standards

Pharmaceutical compounds of analytical grade were purchased from Sigma-Aldrich for sulfamethoxazole (SMX), trimethoprim (TMP), atenolol (ATN), and diclofenac (DCF). Stock solutions of individual pharmaceuticals at a concentration of 150 mg L^{-1} were prepared every 2 days in Milli-Q water and stored in the dark at 4 °C. Working solutions were freshly prepared daily for sorption experiments or analysis.

Humic substances preparation

Extraction and fractionation of sediment humic substances

In sediment HS case, HS were extracted from the sediment following a modified version of the extraction scheme defined by the International Humic Substances Society (IHSS) for soil. Briefly, 160 g of sediment was mixed with 16 mL of H_3PO_4 at 0.3 M to solubilize carbonate. The mixture was shaken for 4 h and the supernatant was collected by centrifugation at 12,000*g*. Then, 32 mL of NaOH at 0.1 M (pH 12) was added to the sediment under a nitrogen stream to avoid oxidation of phenolic groups. The mixture was shaken for 12 h more and the supernatant was collected by centrifugation. The two supernatants were pooled and then diluted in 10 L of Milli-Q water.

After adjustment to pH = 2, HS were finally extracted by sorption on a glass column filled with 250 ml of XAD 8 resin (Supelco) (Thurman and Malcolm 1981). At pH = 2, the sediment humic substances (sediment HS) were retained on the XAD 8 resin whereas the fraction not retained on the resin corresponds to the non-humic substances. HS were recovered from the resin with a solution of acetonitrile in water (75:25, *v*/*v*). Acetonitrile was finally evaporated in a rotary evaporator and then, HS were freeze-dried. The proportions of extracted fractions are then calculated by reference to the total DOC content of the sample.

Aldrich HS preparation

Aldrich HS was chosen to study a HS from another origin, and non-sedimentary humic substances were purchased from Sigma Aldrich. The Aldrich humic acid is known to represent a good model for humic substances and is frequently used as a reference organic matter (Bob and Walker 2001). These HS are extracted from coal by base extraction. A stock solution of Aldrich HS was prepared from the dissolution of 10 g in 1 L of Milli-Q water. The pH was then adjusted to 12 with NaOH 1 M and humines were removed by centrifugation at 12,000*g* for 10 min. The supernatant was acidified at pH 2 with H_3PO_4 and filtered on a 0.45-μm PVDF membrane. The final solution was freeze-dried.

Fresh stock solutions of sediment HS or Aldrich HS were prepared before each series of experiments.

Humic substances characterization

Flash pyrolysis-gas chromatography/mass spectrometry was used to confirm the presence of differences in the composition between the two HS. Results were presented in SI (Fig. SI). Briefly, a quartz reaction tube was packed with 1 mg of dry sample and short quartz wool. The tube is then placed into the platinum filament of the Pyroprobe 1000 pyrolyzer (Chemical Data Systems, Oxford, Pa.). Upon rapid heating at high temperature (50 to 650 °C at 20 °C ms^{-1}), organic matter is degraded into low molecular weight thermal decomposition products.

Separation and identification of pyrolysis products were performed on a Hewlett Packard 5890 Series II Plus gas chromatograph coupled to a mass spectrometer (HP 5972 operating at 70 eV). The system is equipped with a BP 20 (SGE Analytical Science) fused silica capillary column (30 m, 0.25 mm i.d. with 1.0 μm of film thickness). The injector temperature was 280 °C, and the detector temperature was 300 °C. The oven was programmed with an initial temperature of 50 °C, and the temperature was ramped to 240 °C at 4 °C min^{-1} and held for 2 min. Helium was used as the carrier gas at a constant flow rate of 1.0 mL min^{-1}.

Sorption of pharmaceuticals onto the sediment

Sorption procedure

Sorption experiments were performed in 50-mL centrifugation tubes from 1 g of sediment in contact with 4 mL of MilliQ water. Tubes were then horizontally shaken for 24 h in the dark at 25 °C. After this equilibration period, 1 mL of pharmaceutical solution was added to reach the initial concentration for the isotherm (0.3, 0.6, 1.5, 3.0, and 6.0 mg L^{-1}) and then, tubes were re-shaken for 24 h. One milliliter of supernatant was sampled, centrifuged (12,000*g* for 10 min), and filtered on 0.45-μm PVDF filter (Mini-Uni prepTM, Millipore, USA). Finally, the filtrate was diluted 200 times in a water/

MeOH solution (90/10, *v*/*v*) prior to UHPLC-MS/MS analysis. Two tubes (i.e., repetition) were performed for each condition. The pH of these experiments was free but systematic measurements showed that it stayed at 7.1 during the experiments, i.e., the pH value of the Clain river sediment.

Effect of dissolved organic matter

Other sorption experiments were carried out in the presence of sediment HS or Aldrich HS. The amount of HS added (~ 100 mg C L^{-1}) was similar to the water-soluble sediment carbon (WSSC ~ 85 mg C L^{-1}) extracted of sediment by MilliQ water. Thus, after the equilibration period (see sorption procedure described above), the supernatant was centrifuged (12,000*g* for 5 min) and replaced by 4 mL of HS. Then, 1 mL of pharmaceutical solution was added to reach the same concentrations than those applied in the absence of HS. Tubes were re-shaken for 24 h. Finally, the supernatant was collected, centrifuged, and filtered on 0.45-μm PVDF filter for UHPLC-MS/MS analysis.

Dissolved organic carbon (DOC) content was measured with a TOC V-CSH analyzer (Shimadzu). Specific UV absorbance (SUVA) was calculated from the UV absorbance of the solution at 254 nm (CaryUV 50, Agilent) divided by the dissolved organic carbon content.

Pharmaceutical analysis

Pharmaceuticals were separated by high-pressure liquid chromatography on an Acquity UPLC®BEH C18 column (2.1 × 100 mm, 1.7 μm; Waters) with methanol/water both acidified with 0.3% formic acid. The liquid chromatography was coupled to a Q-Exactive Orbitrap™ mass spectrometer (Thermo Fisher Scientific) that combines high-performance quadrupole precursor selection with high-resolution/accurate-mass detection. All pharmaceuticals were detected using an electrospray ion source operating in positive mode. Data acquisition and processing were done using Xcalibur 2.2 software (Thermo Fisher Scientific). Quantification was done according to the external standard method.

Complementary information about the parameters used for pharmaceutical analysis is given in Supplementary material (Table SI-2).

Sorption isotherm models

Four "classical" models were used to describe the sorption data because the isotherm patterns were shown either linear or non-linear:

- The linear model: $Qe = K_d . Ce$

where Qe (mg kg^{-1}) is the solid-phase equilibrium concentration, Ce (mg L^{-1}) is the aqueous phase equilibrium concentration, and Kd is the distribution coefficient in the linear model.

- The Freundlich model: $Qe = K_F . Ce^{1/n}$

where K_F (L kg^{-1}) is the Freundlich distribution coefficient and n is a parameter related to the adsorption intensity.

- The Langmuir model: $Qe = \frac{K_L . Q\max . Ce}{1 + K_L . Ce}$

where K_L (L kg^{-1}) is the Langmuir distribution coefficient and Q_{max} is the maximum adsorption capacity (mg kg^{-1}).

- The Brunauer, Emmett et Teller (BET) model:

$$Qe = qm \frac{K_S . Ce . \left[1 - (n+1)(K_l . Ce)^n + n(K_l . Ce)^{n+1}\right]}{(1 - K_l . Ce) . \left[1 + \left(\frac{K_S}{K_l} - 1\right) K_l . Ce - \left(\frac{K_S}{K_l}\right) . (K_l . Ce)^{n+1}\right]}$$

where K_s and K_l are the equilibrium constants of adsorption for the first layer and for upper layers, respectively, and n is the number of layers. For $n = 1$, the BET model corresponds to the Langmuir model equation.

The sorption model parameters were determined by using the Sigma Plot software package (fit module).

DOM pharmaceutical association in solution

To determine affinity between pharmaceuticals and DOM, the fluorescence quenching method was used (Yamamoto et al. 2003, 2005; Métivier et al. 2013). Thus, solutions of DOM (Aldrich HS, sediment HS, WSSC, and mix between them) were prepared at 5 mg C L^{-1} in a pH = 7 phosphate buffer (25 mM NaH_2PO_4 + 25 mM Na_2HPO_4). Then, DOM solutions were supplied with various concentrations of pharmaceutical (from 0 to 30 mg L^{-1}). After pharmaceutical addition, the solution was shaken for 30 min to reach equilibrium of interaction between DOM and pharmaceutical. Two replicates were performed. Then, fluorescence emission-excitation matrix (EEM) of these solutions was measured with a spectrofluorometer FluoroMax-4 (Horiba Jobin Yvon). EEM was collected with an excitation increment scan at 5 nm within an excitation range of 230–400 nm and an emission range of 300–550 nm with a 1-nm increment. The excitation and emission slit was set at 10 nm, while the scanning speed was set on fast with high sensitivity. Measurements were performed with a 150 W Xenon lamp in a 1.0-cm quartz cuvette at 20 ± 1 °C.

One fluorescence region sensitive to the addition of the different pharmaceuticals was observed for the fluorescence

quenching study. This region is located in the humic-like peak or peak A depicted by Chen et al. (2003).

Fluorescence intensity of the peak A was analyzed using the Stern-Volmer equation:

$$F_0/F = 1 + K_{aff}.Ce$$

where F_0 and F are the fluorescence intensities in the absence and presence of pharmaceutical, respectively, and K_{aff} is the Stern-Volmer constant (binding constant) and Ce the concentration of pharmaceutical.

Results and discussion

Sorption of pharmaceuticals onto the sediment

The sorption experiments performed onto the Clain river sediment highlighted different behavior for the four pharmaceuticals (Fig. 1). Thus, the most important sorption is observed for TMP and then for ATN (Kd = 282 and 137 L kg^{-1}, respectively). On the contrary, the sorption is low for DCF and SMX (Kd = 9 and 3 L kg^{-1}, respectively). It should be noted that only few studies report Kd values for the sorption of these compounds onto sediment, unlike soils. Thus, Pereira Leal et al. (2013) reported Kd values from 0.7 to 28.2 L kg^{-1} for SMX in 13 Brazilian soils. The content of organic matter is generally correlated with the sorption of this compound. For example, Drillia et al. (2005) found for SMX Kd of 37.2 and 0.28 L kg^{-1} for soils with 7.1 and 0.42% of organic matter. These authors have also noted a significant influence of the OM content for DCF (Kd values from 164.5 L kg^{-1} at 7.1% of OM to 0.45 L kg^{-1} at 0.42% of OM).

An overview of literature data did not suggest a "conventional" high sorption of TMP and ATN onto soils or sediment, like it is observed for the Clain sediment. Thus, Lin and Gan (2011) observed Kd values that do not exceed 7.4 L kg^{-1} and Zhang et al. (2014) of 6.73–9.21 L kg^{-1} in soils for TMP. Many works observed generally low Kd values for ATN in river sediments: 8.1 L kg^{-1} Yamamoto et al. (2005); 1.3–8.1 L kg^{-1} (Yamamoto et al. 2009); 7.93 (Martínez-Hernández et al. 2014); 0.85–4 L kg^{-1} (Schaffer et al. 2012) et 9.31 L kg^{-1} (Al-Khazrajy and Boxall 2016) in a range of pH from 6.2 to 8.7.

The pKa of the pharmaceuticals tested are ATN = 9.6, TMP = 7.2, SMX = 5.6, and DCF = 4.1. Thus, the difference of physicochemical properties (see Table SI-3 in supplementary material) between the four pharmaceuticals could explain their different behavior because the pH of sorption experiment was 7.1.

The results suggest that the presence of negative species of SMX and DCF disadvantages the sorption onto the sediment, which the inorganic and organic sediment particles are negatively charged at the pH values of natural waters. On the contrary, the absence of charge for ATN and TMP might lead to less repulsion with the sediment constituents. Kulshrestha et al. (2004) indicated that different species involved different mechanism for pharmaceutical sediment interactions. Thus, cation exchange has been proven to be the most important mechanism for the sorption of pharmaceutical cation species, while for the zwitterion species, surface complexation and hydrophobic interactions are important (Pan et al. 2009).

It is worth noting that no significant relation (R^2 = 0.23, see Fig. SI-2) was observed between the Kd values and the log P of pharmaceuticals, suggesting that hydrophobic interaction is not the principal mechanism of sorption onto the Clain river sediment.

Sorption of pharmaceuticals in the presence of humic substances

Sorption experiments performed in the presence of HS show a change of the sorption of the four compounds (Fig. 2). Three

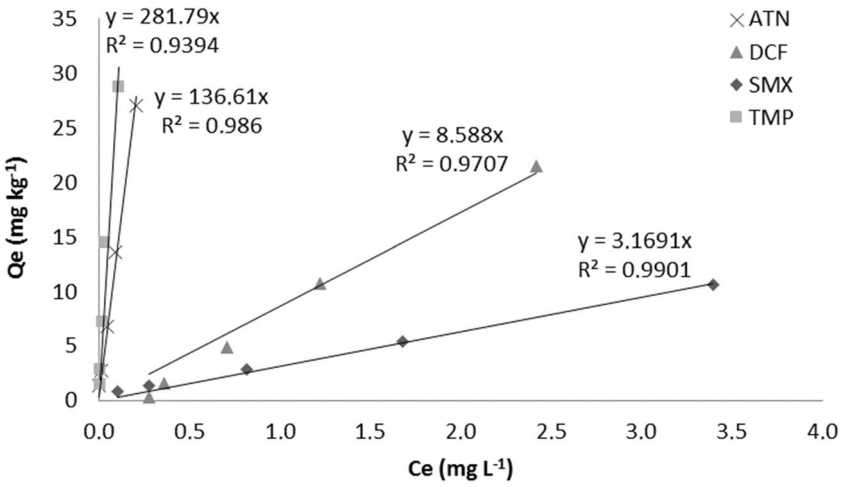

Fig. 1 Sorption isotherms of atenolol (ATN), diclofenac (DCF), sulfamethoxazole (SMX), and trimethoprim (TMP) onto the Clain sediment. Equations and R-squared (R^2) refer to the linear model of sorption

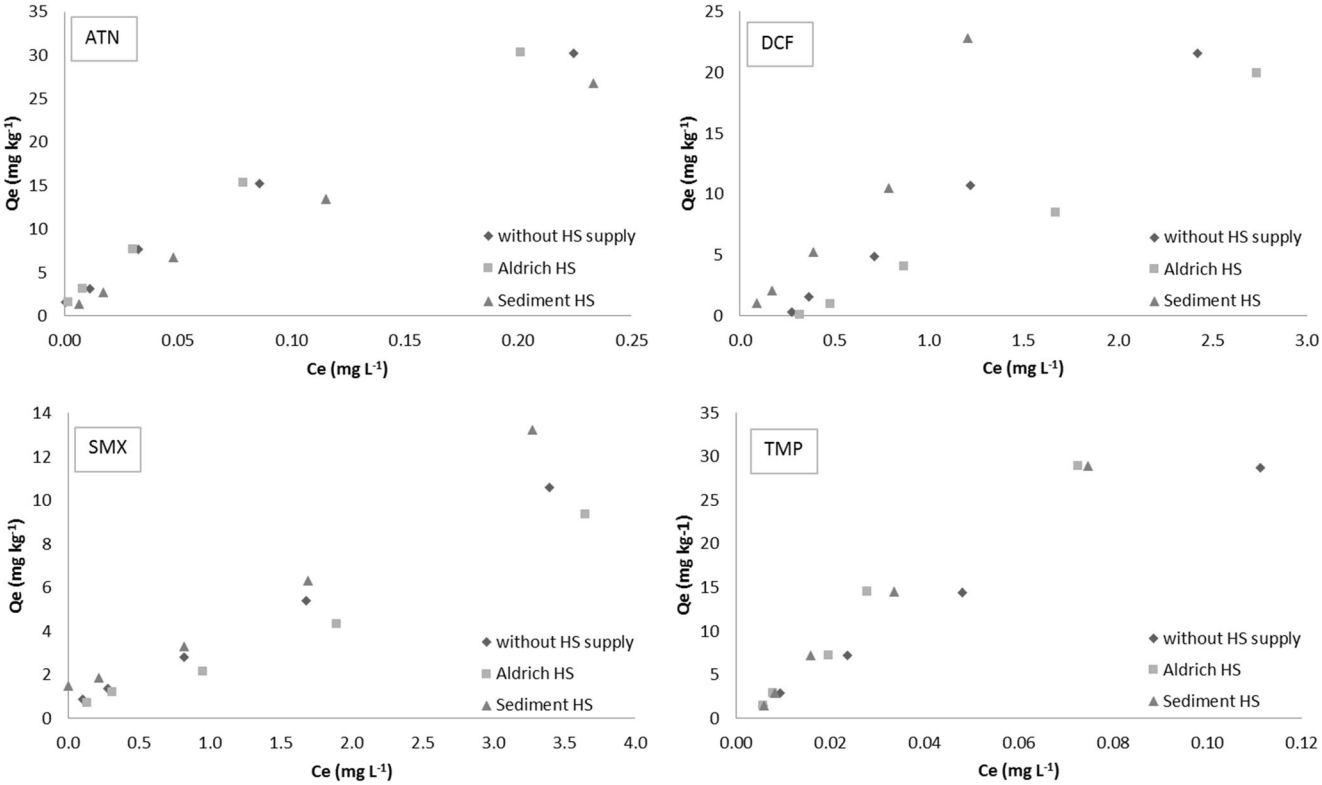

Fig. 2 Isotherms for sorption of atenolol (ATN), diclofenac (DCF), sulfamethoxazole (SMX), and trimethoprim (TMP) onto the Clain sediment in the presence or absence of Aldrich HS or sediment HS

different behaviors were observed. For SMX and DCF (pKa < pH), the presence of Aldrich HS decreases the sorption whereas the presence of sediment HS increase it. Thus, $Kd_{SMX} = 2.5$ and 3.8 L kg^{-1} with Aldrich HS and sediment HS, respectively, and $Kd_{DCF} = 7.1$ and 17 L kg^{-1}, respectively. On the other hand, the sorption of TMP (pKa ≈ pH) was increased in the presence of Aldrich HS ($Kd_{TMP} = 414.9$ L kg^{-1}) or sediment HS ($Kd_{TMP} = 395.9$ L kg^{-1}). The presence of Aldrich HS slightly increases the sorption of ATN (pKa > pH) whereas the presence of sediment HS decreases it. Thus, $Kd_{ATN} = 158.2$ and 108.5 L kg^{-1} with Adrich HS and sediment HS, respectively. All these findings exhibit that HS may have an enhancing or a limiting effect on the sorption of pharmaceuticals. Oh et al. (2016) reported also that ibuprofen can be more easily sorbed onto river sediments in environment simulating low DOM concentrations. Other studies observed that the presence of DOM decrease the sorption of oxytetracycline on clays (Kulshrestha et al. 2004). Similar conclusions were also reported for the sorption of pharmaceuticals onto different solids (activated carbons, clays, biochar) (de Ridder et al. 2011; Lin et al. 2017). All these different works confirm that the formation of pharmaceutical DOM associations can affect sorption. Thus, the presence of DOM may disturb the sorption by acting through direct competition with the pharmaceuticals (i.e., formation of pharmaceutical DOM associations with low affinity for sediment particles) or by blocking the pharmaceuticals accessibility to sites (Gu et al. 2007). The difference observed between the two HS are probably related to their different physicochemical properties (including binding affinity, charges, hydrophobicity…) that may occur in the sorption phenomena.

The results also highlight that the effect of HS depends strongly on their origin. It is worth noting that the HS "native" from the sediment induces no "specific" effect on the sorption of the studied pharmaceuticals. No systematic increase or decrease was observed with the sediment HS. Consequently, the formation of HS in sediment or their remobilization (e.g., during floods or storm events) impacts differently the ability of the Clain river sediment to sorb each pharmaceutical.

Study of the sorption mechanisms

Sorption isotherm models

Classical sorption models were used to describe sorption data and to highlight changes in the sorption mechanisms induced by the presence of HS (Table 1).

This approach by "models" was first performed on sorption isotherm realized without HS supply. The sorption isotherms of the four pharmaceuticals are well described by the linear model and the Freundlich model in concordance of literature. Thus, the linear isotherm model was frequently

Table 1 Binding constants and other sorption parameters determined from the linear Freundlich, Langmuir, and BET models. Standard deviation given into brackets corresponds to the error given by the model (*Ab. value* aberrant value). Full data are available in complementary data file

		Linear model		Freundlich model			Langmuir model			BET model				
		Kd L kg^{-1}	R^2	n	K_F $mg^{1-1/n}$ $L^{1/n}$ kg^{-}	r^2	K_L L mg^{-1}	Q_{max} mg kg^{-1}	R^2	Qm mg kg^{-1}	Ks L mg^{-}	K_l L kg^{-1}	n	R^2
DCF	Without HS supply	9.9 (0.3)	0.997	0.83 (0.08)	7.5 (0.7)	0.988	Ab.val	Ab.val	0.976	10 (1)	1.8 (0.9)	1.1 (0.4)	3	0.998
	Aldrich HS	8 (0.7)	0.980	0.62 (0.05)	3.9 (0.5)	0.994	Ab.val	Ab.val	0.918	Ab.val	Ab.val	Ab.val	2	0.993
	Sediment HS	18.8 (2.1)	0.963	0.68 (0.08)	17 (0.8)	0.987	Ab.val	Ab.val	0.948	8 (1.25)	1.7 (0.5)	0.57 (0.03)	21	0.999
ATN	Without HS supply	126.5 (8.2)	0.988	1.4 (0.07)	87 (6)	0.997	3.6 (1)	67 (12)	0.994	21 (9)	15 (11)	4.45 (4.78)	4	0.996
	Aldrich HS	142.1 (8.3)	0.990	1.39 (0.03)	96 (3)	0.999	3.7 (1)	70 (13)	0.994	13 (9)	29 (22)	1.8 (0.9)	6	0.998
	Sediment HS	111 (2.1)	0.999	1.11 (0.04)	99 (6)	0.998	0.6 (0.4)	205 (132)	0.997	Ab.val	Ab.val	Ab.val	1	0.999
TMP	Without HS supply	256.6 (11.3)	0.994	1.12 (0.04)	203 (17)	0.998	2.4 (0.4)	135 (18)	0.999	Ab.val	Ab.val	Ab.val	1.7	0.999
	Aldrich HS	408 (3.67)	0.976	1.06 (0.12)	345 (110)	0.978	2.5 (3)	188 (210)	0.980	Ab.val	Ab.val	Ab.val	3	0.977
	Sediment HS	393.6 (19.6)	0.993	1.05 (0.07)	340 (58)	0.994	2.0 (1.5)	222 (153)	0.995	Ab.val	Ab.val	Ab.val	3	0.999
SMX	Without HS supply	3 (0)	1.000	1.12 (0.07)	3.5 (0.2)	0.996	0.04	76 (61)	0.993	2.6 (0.2)	3.2 (0.5)	0.36 (0.03)	6	0.999
	Aldrich HS	2.4 (0.1)	0.989	0.95 (0.1)	2.4 (0.3)	0.988	Ab.val	Ab.val	0.987	1.59 (0.01	5.7 (0.2)	0.36 (0.01)	8	0.999
	Sediment HS	3.6 (0.3)	0.985	1.02 (0.18)	4.1 (0.7)	0.963	Ab.val	Ab.val	0.963	4.8 (2.4)	2.0 (2.9)	0.2 (0.04)	18	0.972

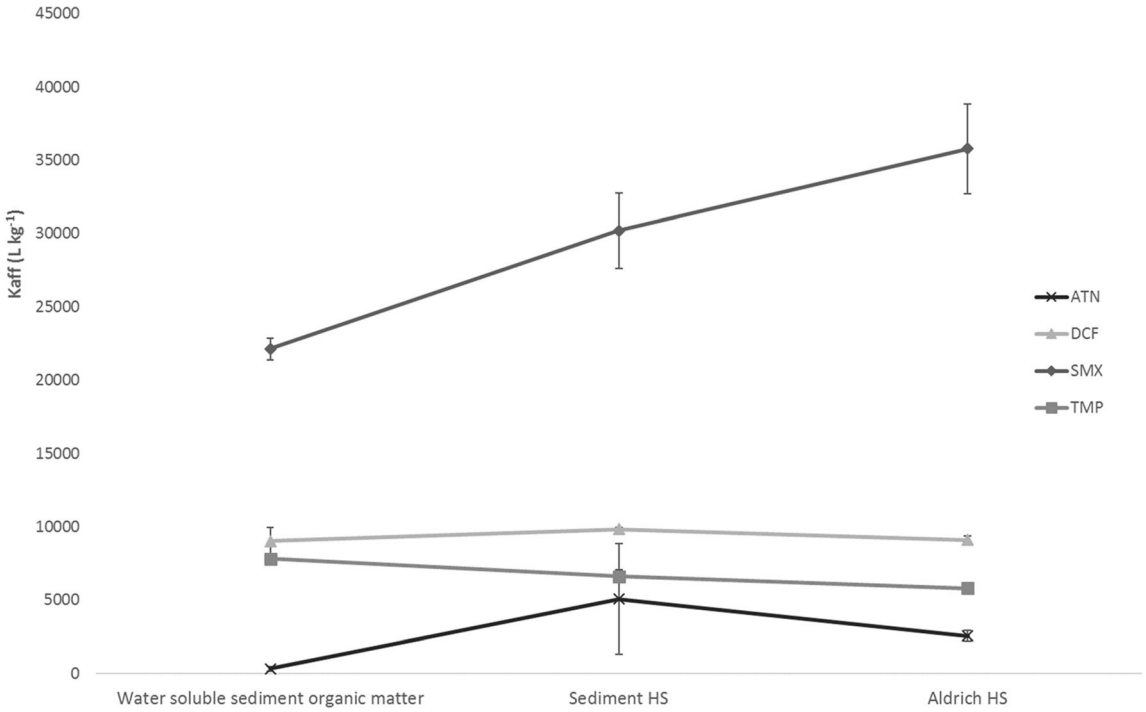

Fig. 3 Binding constants for atenolol (ATN), diclofenac (DCF), sulfamethoxazole (SMX), and trimethoprim (TMP) with water-soluble sediment organic matter and Aldrich or sediment HS. (Standard deviations were obtained from two replicate of fluorescence quenching experiments)

found efficient for the sorption isotherms of several pharmaceuticals onto fine sediments (Drillia et al. 2005; Schaffer et al. 2012; Styszko 2016). Other works (Kim et al. 2007; Ramil et al. 2010; Martínez-Hernández et al. 2014; Radović et al. 2016) pointed out that sorption isotherms of pharmaceuticals onto soils or sediments are better fitted with the Freundlich model. The present results show also that DCF, SMX, and ATN isotherm sorption are also well fitted by the BET model, which suggests a multilayer sorption mechanism. On the contrary, TMP seems to involve a monolayer sorption mechanism as suggested by the Langmuir model. Zhong et al. (2013) found that the Langmuir model described the adsorption process of some pharmaceuticals (e.g., sulfonamides) on river sediments better than the Freundlich model.

The approach by "models" also highlights that the presence of HS does not change drastically the sorption mechanisms. Using the BET model, the Aldrich HS supply does not change the number of sorption layers determined for SMX ($n = 8$ or 6) and DCF ($n = 3$ or 2), but increased when sediment HS were used (from $n = 6$ to 18 and from $n = 1$ to 21 for SMX

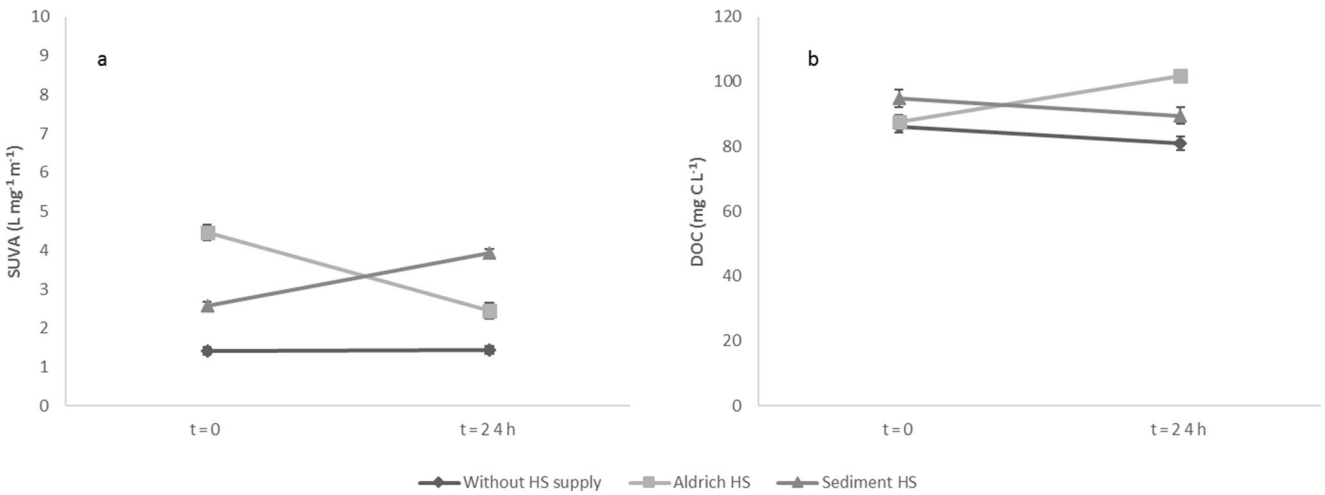

Fig. 4 Evolution of SUVA (**a**) and DOC (**b**) during isotherm experiments performed in the presence or absence of Aldrich or sediment HS. $t = 0$ is collected after 5 min of contact between sediment and solution; $t = 24$ h is collected at the end of the isotherm experiment. (Standard deviations were obtained from three replicate experiments)

and DCF, respectively, Table 1). These findings suggest that the sediment HS favors the formation of multilayers which lead to an increase in the sorption of SMX and DCF. No change was observed for the modelization of the TMP sorption isotherms (i.e., BET model still leads to aberrant values).

The presence of pharmaceutical HS association in solution

The fluorescence measurements showed a significant quenching of the signal of organic matters in the presence of SMX, DCF, and TMP. Thus, binding constants (K_{aff}) could be determined for these three pharmaceuticals, suggesting that they form associations with the Aldrich or sediment HS and also with the WSSC. The results (Fig. 3) exhibit higher binding constants for SMX (22 10^3–36 10^3 L kg^{-1}) than for DCF and TMP (7.2 10^3–9.8 10^3 L kg^{-1} and 4.6 10^3–7.8 10^3 L kg^{-1}, respectively). No significant difference was found between the two studied HS whereas Mori et al. (2010) pointed out different binding affinities to pharmaceuticals for ten different humic materials. The only difference observed concerns the binding constant of SMX which is much higher in the presence of HS than only in the WSSC. No major difference was observed for DCF and TMP.

The results point out also that ATN does not induce quenching with the WSSC. It forms only associations with the Aldrich and sediment HS, but the binding constants are low (3.2 10^2 and 5.1 10^3 L kg^{-1}, respectively). Yamamoto et al. (2005) found also a low binding constant for ATN with the Suwannee river organic matter (1.1 10^2 L kg^{-1}). Nevertheless, other works (Mori et al. 2010) showed that ATN can have high affinity for some humic material.

It is also worth noting that the compounds with the highest binding constants (i.e., pharmaceutical-dissolved organic matter association) have the lowest sorption constants (i.e., Kd values). Consequently, competition effects between DOM and sediment particles seem to play an important role in the sorption of pharmaceuticals onto the Clain river sediment. Other studies have also shown that the presence of co-solute (e.g., HS or model compounds) may affect the sorption or desorption rates of organic contaminants (Xing and Pignatello 1998; Faria and Young 2010). The binding constants did not explain, however, why the sorption onto the sediment can be increased or decreased in the presence of sediment HS or Aldrich HS. Consequently, other mechanisms than competition are probably involved in the sorption onto the Clain river sediment.

Composition of solution

The XAD fractionation protocol used for extraction of the HS provided also an overview of the repartition between humic substances and non-humic substances (i.e., more hydrophilic compounds). Thus, the XAD fractionation highlights that sediment is mainly composed of humic substances (78%). On the contrary, the WSSC is mainly composed of non-humic substances (97%).

These observations reveal that the addition of HS (Aldrich or sediment) widely changes the character of the solution during the sorption experiments. Furthermore, the addition of sediment HS probably re-equilibrates the "organic matter composition" between the sediment and the solution. On the contrary, the addition of Aldrich HS re-equilibrates also the balance of hydrophobic compounds but these HS probably do not have the same affinity/reactivity for this sediment due to their non-sedimentary origin.

The specific UV absorbance values of the solution do not change in the absence of HS whereas the values decrease in the presence of Aldrich HS. This decrease is associated with an increase of the DOC in the solution, which suggests that the Aldrich HS causes a mobilization of organic matter from the sediment to the solution (Fig. 4). On the contrary, the results show also a decrease of the DOC and an increase of the SUVA in the presence of sediment HS. This finding suggests a fixation of sediment HS from the solution onto the sediment. (nb. it was considered that microbial activity was not sufficiently effective/efficient at 24 h.) The sorption of DOC on natural particles has already been highlighted by Vandenbruwane et al. (2007). Consequently, the sorption/desorption of DOM plays probably also an important role in the sorption of pharmaceuticals onto the Clain river sediment. Furthermore, the difference of behavior between the Aldrich HS and the sediment HS is not surprising since preferential interaction between certain components of humic substances (aliphatic vs. aromatic) and mineral phases are reported in the literature (Wang and Xing 2005). Gu et al. (2007) suggest that the stereochemical arrangement of the functional groups on HS may lead to preferential sorption of certain humic fractions.

Conclusion

This work confirmed that the presence of humic substances influences the sorption of pharmaceuticals onto sediments. Thus, the results point out that the presence of sediment HS increases the sorption of SMX, DCF, and TMP, but slightly reduces the sorption of ATN. Similarly, the presence of Aldrich HS causes an increase of the sorption of TMP and ATN and a decrease of the sorption of SMX and DCF. Consequently, there is no "unique effect" induced by the origin of organic matter.

The use of an approach based on "classical sorption models" suggested that the sorption of SMX, DCF, and ATN involves multilayer mechanisms. This approach also pointed out that the presence of HS does not change the sorption mechanisms in the presence of sediment HS or Aldrich HS.

Difference of sorption observed with the two HS was attributed to their behavior with the Clain sediment. Thus, a possible sorption of the sediment HS onto the Clain sediment was suggested from DOC measurements performed during sorption experiments. Such phenomena might be attributed to their common origin which lead probably to strong affinities. On the contrary, the Aldrich HS has shown to induce a mobilization of OM from the sediment to the solution.

The measurements performed by fluorescence quenching supported the presence of pharmaceutical HS associations. However, these associations do not explained increase or decrease in the pharmaceuticals sorption observed with one or the other HS. Indeed, the results point out no major difference of binding constants (K_{app}) between the two HS whereas sorption isotherms report significant difference of the distribution coefficients (Kd).

Finally, this work shows that the sorption of pharmaceuticals is a complex mechanism in which sediment properties, pharmaceutical properties, and DOM origin interact to govern sorption. Furthermore, other elements (e.g., ions, salinity)—not considered in this work—have also an important role in the sorption mechanisms. Thus, mechanistic studies are urgently needed for a better understanding of the implication of each compartment and to develop more pertinent model for prediction of the sorption of pharmaceuticals.

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References

Aga DS (2007) Fate of pharmaceuticals in the environment and in water treatment systems. CRC Press, Boca Raton

Al-Khazrajy OSA, Boxall ABA (2016) Impacts of compound properties and sediment characteristics on the sorption behaviour of pharmaceuticals in aquatic systems. J Hazard Mater 317:198–209. https://doi.org/10.1016/j.jhazmat.2016.05.065

Aus der Beek T, Weber F-A, Bergmann A et al (2016) Pharmaceuticals in the environment—global occurrences and perspectives. Environ Toxicol Chem 35:823–835. https://doi.org/10.1002/etc.3339

Avisar D, Primor O, Gozlan I, Mamane H (2010) Sorption of sulfonamides and tetracyclines to montmorillonite clay. Water Air Soil Pollut 209:439–450. https://doi.org/10.1007/s11270-009-0212-8

Bai Y, Wu F, Liu C, Guo J, Fu P, Li W, Xing B (2008) Interaction between carbamazepine and humic substances: a fluorescence spectroscopy study. Environ Toxicol Chem 27:95–102. https://doi.org/10.1897/07-013.1

Barnes KK, Kolpin DW, Furlong ET, Zaugg SD, Meyer MT, Barber LB (2008) A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States—I groundwater. Sci Total Environ 402:192–200. https://doi.org/10.1016/j.scitotenv.2008.04.028

Bekçi Z, Seki Y, Yurdakoç MK (2006) Equilibrium studies for trimethoprim adsorption on montmorillonite KSF. J Hazard Mater 133:233–242. https://doi.org/10.1016/j.jhazmat.2005.10.029

Bob MM, Walker HW (2001) Effect of natural organic coatings on the polymer-induced coagulation of colloidal particles. Colloids Surf A Physicochem Eng Asp 177:215–222. https://doi.org/10.1016/S0927-7757(00)00679-8

Bradley PM, Journey CA, Button DT, Carlisle DM, Clark JM, Mahler BJ, Nakagaki N, Qi SL, Waite IR, VanMetre PC (2016) Metformin and other pharmaceuticals widespread in wadeable streams of the southeastern United States. Environ Sci Technol Lett 3:243–249. https://doi.org/10.1021/acs.estlett.6b00170

Chen W, Westerhoff P, Leenheer JA, Booksh K (2003) Fluorescence excitation−emission matrix regional integration to quantify spectra for dissolved organic matter. Environ Sci Technol 37:5701–5710. https://doi.org/10.1021/es034354c

Chonova T, Keck F, Labanowski J, Montuelle B, Rimet F, Bouchez A (2016) Separate treatment of hospital and urban wastewaters: a real scale comparison of effluents and their effect on microbial communities. Sci Total Environ 542:965–975. https://doi.org/10.1016/j.scitotenv.2015.10.161

Chonova T, Labanowski J, Cournoyer B, Chardon C, Keck F, Laurent É, Mondamert L, Vasselon V, Wiest L, Bouchez A (2017) River biofilm community changes related to pharmaceutical loads emitted by a wastewater treatment plant. Environ Sci Pollut Res 1–11. https://doi.org/10.1007/s11356-017-0024-0

da Silva BF, Jelic A, López-Serna R et al (2011) Occurrence and distribution of pharmaceuticals in surface water, suspended solids and sediments of the Ebro river basin, Spain. Chemosphere 85:1331–1339. https://doi.org/10.1016/j.chemosphere.2011.07.051

de Ridder DJ, Verliefde ARD, Heijman SGJ, Verberk JQJC, Rietveld LC, van der Aa LTJ, Amy GL, van Dijk JC (2011) Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon. Water Sci Technol 63:416–423. https://doi.org/10.2166/wst.2011.237

de Voogt P, Janex-Habibi M-L, Sacher F, Puijker L, Mons M (2009) Development of a common priority list of pharmaceuticals relevant for the water cycle. Water Sci Technol 59(1):39

Drillia P, Stamatelatou K, Lyberatos G (2005) Fate and mobility of pharmaceuticals in solid matrices. Chemosphere 60:1034–1044. https://doi.org/10.1016/j.chemosphere.2005.01.032

Environmental Protection Agency U.S. (2012) Water: contaminant candidate list 3—CCL

European Commision (2013) Directive 2013/39/EU of the European Parliament and of the council of 12 August 2013 amending directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy (2011/0429 (COD))

Faria IR, Young TM (2010) Modeling and predicting competitive sorption of organic compounds in soil. Environ Toxicol Chem 29:2676–2684. https://doi.org/10.1002/etc.343

Gaw S, Thomas KV, Hutchinson TH (2014) Sources, impacts and trends of pharmaceuticals in the marine and coastal environment. Phil Trans R Soc B 369:20130572. https://doi.org/10.1098/rstb.2013.0572

Gilbert N (2012) Drug-pollution law all washed up. Nature 491:503–504. https://doi.org/10.1038/491503a

Gu C, Karthikeyan KG, Sibley SD, Pedersen JA (2007) Complexation of the antibiotic tetracycline with humic acid. Chemosphere 66:1494–1501. https://doi.org/10.1016/j.chemosphere.2006.08.028

Hernandez-Ruiz S, Abrell L, Wickramasekara S, Chefetz B, Chorover J (2012) Quantifying PPCP interaction with dissolved organic matter in aqueous solution: combined use of fluorescence quenching and tandem mass spectrometry. Water Res 46:943–954. https://doi.org/10.1016/j.watres.2011.11.061

Hu X, He K, Zhou Q (2012) Occurrence, accumulation, attenuation and priority of typical antibiotics in sediments based on long-term field and modeling studies. J Hazard Mater 225–226:91–98. https://doi.org/10.1016/j.jhazmat.2012.04.062

Kasprzyk-Hordern B, Kondakal VVR, Baker DR (2010) Enantiomeric analysis of drugs of abuse in wastewater by chiral liquid chromatography coupled with tandem mass spectrometry.

J Chromatogr A 1217:4575–4586. https://doi.org/10.1016/j.chroma.2010.04.073

Kim I, Yu Z, Xiao B, Huang W (2007) Sorption of male hormones by soils and sediments. Environ Toxicol Chem 26:264–270. https://doi.org/10.1897/06-270R1.1

Klosterhaus SL, Grace R, Hamilton MC, Yee D (2013) Method validation and reconnaissance of pharmaceuticals, personal care products, and alkylphenols in surface waters, sediments, and mussels in an urban estuary. Environ Int 54:92–99. https://doi.org/10.1016/j.envint.2013.01.009

Kulshrestha P, Giese Rossman F, Aga DS (2004) Investigating the molecular interactions of oxytetracycline in clay and organic matter: insights on factors affecting its mobility in soil. Environ Sci Technol 38:4097–4105. https://doi.org/10.1021/es034856q

Kümmerer K (2009) Antibiotics in the aquatic environment—a review—part I. Chemosphere 75:417–434. https://doi.org/10.1016/j.chemosphere.2008.11.086

Kunkel U, Radke M (2012) Fate of pharmaceuticals in rivers: deriving a benchmark dataset at favorable attenuation conditions. Water Res 46:5551–5565. https://doi.org/10.1016/j.watres.2012.07.033

Lai KM, Johnson KL, Scrimshaw MD, Lester JN (2000) Binding of waterborne steroid estrogens to solid phases in river and estuarine systems. Environ Sci Technol 34:3890–3894. https://doi.org/10.1021/es9912729

Langford K, Thomas KV (2011) Input of selected human pharmaceutical metabolites into the Norwegian aquatic environment. J Environ Monit 13:416–421. https://doi.org/10.1039/C0EM00342E

Lei B, Huang S, Zhou Y, Wang D, Wang Z (2009) Levels of six estrogens in water and sediment from three rivers in Tianjin area, China. Chemosphere 76:36–42. https://doi.org/10.1016/j.chemosphere.2009.02.035

Lewandowski J, Putschew A, Schwesig D, Neumann C, Radke M (2011) Fate of organic micropollutants in the hyporheic zone of a eutrophic lowland stream: results of a preliminary field study. Sci Total Environ 409:1824–1835. https://doi.org/10.1016/j.scitotenv.2011.01.028

Li J, Zhang H (2016) Adsorption-desorption of oxytetracycline on marine sediments: kinetics and influencing factors. Chemosphere 164:156–163. https://doi.org/10.1016/j.chemosphere.2016.08.100

Li Z, Sobek A, Radke M (2016) Fate of pharmaceuticals and their transformation products in four small European rivers receiving treated wastewater. Environ Sci Technol 50:5614–5621. https://doi.org/10.1021/acs.est.5b06327

Liang X, Chen B, Nie X, Shi Z, Huang X, Li X (2013) The distribution and partitioning of common antibiotics in water and sediment of the Pearl River Estuary, South China. Chemosphere 92:1410–1416. https://doi.org/10.1016/j.chemosphere.2013.03.044

Lin K, Gan J (2011) Sorption and degradation of wastewater-associated non-steroidal anti-inflammatory drugs and antibiotics in soils. Chemosphere 83:240–246. https://doi.org/10.1016/j.chemosphere.2010.12.083

Lin L, Jiang W, Xu P (2017) Comparative study on pharmaceuticals adsorption in reclaimed water desalination concentrate using biochar: impact of salts and organic matter. Sci Total Environ 601:857–864. https://doi.org/10.1016/j.scitotenv.2017.05.203

Martínez-Hernández V, Meffe R, Herrera S, Arranz E, de Bustamante I (2014) Sorption/desorption of non-hydrophobic and ionisable pharmaceutical and personal care products from reclaimed water onto/from a natural sediment. Sci Total Environ 472:273–281. https://doi.org/10.1016/j.scitotenv.2013.11.036

Matongo S, Birungi G, Moodley B, Ndungu P (2015) Occurrence of selected pharmaceuticals in water and sediment of Umgeni River, KwaZulu-Natal, South Africa. Environ Sci Pollut Res 22:10298–10308. https://doi.org/10.1007/s11356-015-4217-0

Mennigen JA, Stroud P, Zamora JM, Moon TW, Trudeau VL (2011) Pharmaceuticals as neuroendocrine disruptors: lessons learned from fish on Prozac. J Toxicol Environ Health B 14:387–412. https://doi.org/10.1080/10937404.2011.578559

Métivier R, Bourven I, Labanowski J, Guibaud G (2013) Interaction of erythromycin ethylsuccinate and acetaminophen with protein fraction of extracellular polymeric substances (EPS) from various bacterial aggregates. Environ Sci Pollut Res 20:7275–7285. https://doi.org/10.1007/s11356-013-1738-2

Mori H, Ohtani T, Fukuda I, et al (2010) Sorption of pharmaceuticals to humic substances. In: Advances in natural organic matter and humic substances research 2008–20100. J.A. González-Pérez, F.J. González-Vila, G. Almendros, Puerto de la Cruz, Tenerife, Canary Islands, pp 182–185

Oh S, Shin WS, Kim HT (2016) Effects of pH, dissolved organic matter, and salinity on ibuprofen sorption on sediment. Environ Sci Pollut Res 23:22882–22889. https://doi.org/10.1007/s11356-016-7503-6

Okuda T, Kobayashi Y, Nagao R, Yamashita N, Tanaka H, Tanaka S, Fujii S, Konishi C, Houwa I (2008) Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan. Water Sci Technol 57:65–71. https://doi.org/10.2166/wst.2008.822

Padhye LP, Yao H, Kung'u FT, Huang C-H (2014) Year-long evaluation on the occurrence and fate of pharmaceuticals, personal care products, and endocrine disrupting chemicals in an urban drinking water treatment plant. Water Res 51:266–276. https://doi.org/10.1016/j.watres.2013.10.070

Pan B, Ning P, Xing B (2009) Part V—sorption of pharmaceuticals and personal care products. Environ Sci Pollut Res 16:106–116. https://doi.org/10.1007/s11356-008-0052-x

Peng N, Wang K, Liu G, Li F, Yao K, Lv W (2014) Quantifying interactions between propranolol and dissolved organic matter (DOM) from different sources using fluorescence spectroscopy. Environ Sci Pollut Res 21:5217–5226. https://doi.org/10.1007/s11356-013-2436-9

Pereira Leal RM, Ferracciu Alleoni LR, Tornisielo VL, Regitano JB (2013) Sorption of fluoroquinolones and sulfonamides in 13 Brazilian soils. Chemosphere 92:979–985. https://doi.org/10.1016/j.chemosphere.2013.03.018

Pinckney JL, Hagenbuch IM, Long RA, Lovell CR (2013) Sublethal effects of the antibiotic tylosin on estuarine benthic microalgal communities. Mar Pollut Bull 68:8–12. https://doi.org/10.1016/j.marpolbul.2013.01.006

Radke M, Maier MP (2014) Lessons learned from water/sediment-testing of pharmaceuticals. Water Res 55:63–73. https://doi.org/10.1016/j.watres.2014.02.012

Radke M, Ulrich H, Wurm C, Kunkel U (2010) Dynamics and attenuation of acidic pharmaceuticals along a river stretch. Environ Sci Technol 44:2968–2974. https://doi.org/10.1021/es903091z

Radović TT, Grujić SD, Kovačević SR, Laušević MD, Dimkić MA (2016) Sorption of selected pharmaceuticals and pesticides on different river sediments. Environ Sci Pollut Res 23:25232–25244. https://doi.org/10.1007/s11356-016-7752-4

Ramil M, El Aref T, Fink G et al (2010) Fate of beta blockers in aquatic-sediment systems: sorption and biotransformation. Environ Sci Technol 44:962–970. https://doi.org/10.1021/es9027452

Riml J, Wörman A, Kunkel U, Radke M (2013) Evaluating the fate of six common pharmaceuticals using a reactive transport model: insights from a stream tracer test. Sci Total Environ 458–460:344–354. https://doi.org/10.1016/j.scitotenv.2013.03.077

Schaffer M, Boxberger N, Börnick H, Licha T, Worch E (2012) Sorption influenced transport of ionizable pharmaceuticals onto a natural sandy aquifer sediment at different pH. Chemosphere 87:513–520. https://doi.org/10.1016/j.chemosphere.2011.12.053

Styszko K (2016) Sorption of emerging organic micropollutants onto fine sediments in a water supply dam reservoir, Poland. J Soils Sediments 16:677–686. https://doi.org/10.1007/s11368-015-1239-7

Sun WL, Ni JR, Liu TT (2006) Effect of sediment humic substances on sorption of selected endocrine disruptors. Water Air Soil Pollut Focus 6:583–591. https://doi.org/10.1007/s11267-006-9043-4

Sun WL, Ni JR, Xu N, Sun LY (2007) Fluorescence of sediment humic substance and its effect on the sorption of selected endocrine disruptors. Chemosphere 66:700–707. https://doi.org/10.1016/j.chemosphere.2006.07.078

Tamtam F, Bot BL, Dinh T et al (2011) A 50-year record of quinolone and sulphonamide antimicrobial agents in Seine River sediments. J Soils Sediments 11:852–859. https://doi.org/10.1007/s11368-011-0364-1

Thurman EM, Malcolm RL (1981) Preparative isolation of aquatic humic substances. Environ Sci Technol 15:463–466. https://doi.org/10.1021/es00086a012

Vandenbruwane J, De Neve S, Qualls RG et al (2007) Comparison of different isotherm models for dissolved organic carbon (DOC) and nitrogen (DON) sorption to mineral soil. Geoderma 139:144–153. https://doi.org/10.1016/j.geoderma.2007.01.012

Varga M, Dobor J, Helenkár A, Jurecska L, Yao J, Záray G (2010) Investigation of acidic pharmaceuticals in river water and sediment by microwave-assisted extraction and gas chromatography–mass spectrometry. Microchem J 95:353–358. https://doi.org/10.1016/j.microc.2010.02.010

Wang K, Xing B (2005) Structural and sorption characteristics of adsorbed humic acid on clay minerals. J Environ Qual 34:342–349. https://doi.org/10.2134/jeq2005.0342

Xing B, Pignatello JJ (1998) Competitive sorption between 1,3-dichlorobenzene or 2,4-dichlorophenol and natural aromatic acids in soil organic matter. Environ Sci Technol 32:614–619. https://doi.org/10.1021/es9704646

Yamamoto H, Liljestrand HM, Shimizu Y, Morita M (2003) Effects of physical−chemical characteristics on the sorption of selected endocrine disruptors by dissolved organic matter surrogates. Environ Sci Technol 37:2646–2657. https://doi.org/10.1021/es026405w

Yamamoto H, Hayashi A, Nakamura Y, Sekizawa J (2005) Fate and partitioning of selected pharmaceuticals in aquatic environment. Environ Sci 12:347–358

Yamamoto H, Nakamura Y, Moriguchi S, Nakamura Y, Honda Y, Tamura I, Hirata Y, Hayashi A, Sekizawa J (2009) Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: laboratory photolysis, biodegradation, and sorption experiments. Water Res 43:351–362. https://doi.org/10.1016/j.watres.2008.10.039

Zhang R, Zhang F, Zhang T, Yan H, Shao W, Zhou L, Tong H (2014) Historical sediment record and distribution of polychlorinated biphenyls (PCBs) in sediments from tidal flats of Haizhou Bay, China. Mar Pollut Bull 89:487–493. https://doi.org/10.1016/j.marpolbul.2014.09.001

Zhong Z, Xu J, Zhang Y, Li L, Guo C, He Y, Fan W, Zhang B (2013) Adsorption of sulfonamides on lake sediments. Front Environ Sci Eng 7(4):518–525

Zhou L-J, Ying G-G, Zhao J-L, Yang JF, Wang L, Yang B, Liu S (2011) Trends in the occurrence of human and veterinary antibiotics in the sediments of the Yellow River, Hai River and Liao River in northern China. Environ Pollut 159:1877–1885. https://doi.org/10.1016/j.envpol.2011.03.034